Be it known, that we, **Himiko Takayama and Katsumi Umehara**, both residing in Shizuoka, Japan and both citizens of Japan; have invented new and useful improvements in a

LUBRICATING OIL COMPOSITION HAVING EXCELLENT THERMAL STABILITY, EXTREME PRESSURE RESISTANCE AND ANTI-WEAR PERFORMANCE

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LUBRICATING OIL COMPOSITION HAVING EXCELLENT THERMAL STABILITY, EXTREME PRESSURE RESISTANCE AND ANTI-WEAR PERFORMANCE

The present invention relates to a lubricating oil composition for use in industrial oils such as hydraulic oils, bearing oils, industrial gear oils and sliding surface lubricating oils. The lubricating oil composition of the present invention provides excellent thermal stability, extreme pressure resistance and anti-wear performance.

BACKGROUND OF THE INVENTION

The technology that is normally responsible for separating the applications of lubricants is anti-wear or extreme pressure (EP) chemistry. The distinction between anti-wear and EP is difficult to define but anti-wear is in general based on the prevention of damage caused by moderate and intermittent loadings whereas EP is the protection from shock loadings and continually applied heavy or sliding loads. Two types of chemistry have evolved around these needs. EP and anti-wear protection are typically provided by "ash-containing" components such as zinc dithiophosphates (ZnDTP). ZnDTP are commonly employed as additives in lubricating oils primarily for their excellent extreme pressure and anti-wear properties. However, ZnDTP may decompose at high operating temperatures and produce sludge that can contribute to filter plugging and viscosity increase of the lubricating oil. The other type of chemistry involves "ashless" sulfur and phosphorus chemistry. The reference to ash containing or ashless chemistry is historical and there are now ashless alternatives to ZnDTP. Generally, phosphorus-containing anti-wear agents have excellent thermal stability under conditions of high temperature operation as demanded, for instance, in industrial oils such as hydraulic oil, bearing oil, industrial gear oil and sliding surface lubricating oil. But, extreme pressure and anti-wear performance is relatively poor in comparison to ZnDTP. Thus, in practice ZnDTP-free lubricating oils combining thermal stability, extreme pressure resistance and anti-wear performance are rare. It is not easy to produce lubricating oils having

thermal stability at high temperatures with concomitant extreme pressure and anti-wear performance.

Japanese Patent Provisional Publication No. 9-111277 describes an ashless hydraulic oil composition comprising a base oil having a % C_A (percentage that represents the number of carbon atoms in aromatic groups divided by total carbon atoms) 5 or less, (A) 0.01-5 wt % of an amine-type oxidation inhibitor, (B) 0.01-5 wt % of a phenolic oxidation inhibitor, (C) 0.01-5 wt % of a phosphoric acid ester, and (D) 0.001-5 wt % of an aliphatic amide and/or a polyhydric alcohol ester.

Japanese Patent Provisional Publication No. 11-323365 describes a hydraulic oil using a mineral oil, a synthetic oil, or a mixture thereof, as a base oil, which further contains (A) 0.01-1 wt % of an alkenyl succinimide or its derivative, (B) 0.1-5 wt % of a phosphoric acid ester, (C) 0.05-0.5 wt % of an alkylated diphenylamine, and (D) 0.05-0.5 wt % of a hindered phenol.

SUMMARY OF THE INVENTION

The present invention relates to a lubricating oil composition for use in industrial oils such as hydraulic oils, bearing oils, industrial gear oils and sliding surface lubricating oils. The lubricating oil composition of the present invention provides excellent thermal stability, extreme pressure resistance and anti-wear performance.

In its broadest aspect, the present invention relates to a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity and

A. 0.1 to 5.0 wt % of at least one compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof;

B. 0.01 to 1.0 wt % of a phosphorus acid ester and/or an amine thereof; and

C. 0.01 to 2.0 wt % of at least one compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof.

The weight ratio between the compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof and the phosphorus acid ester and/or an amine thereof is in the range of 1:1 to 500:1.

The weight ratio between the phosphoric acid ester and/or an amine thereof and the compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof is in the range of 1:0.5 to 1:20.

The lubricating oil composition of the present invention has a total phosphorus content in the range of 50 to 5,000 mass ppm.

In another aspect, the present invention relates to a lubricating oil concentrate containing a compatible organic diluent and

A. 10 to 90 wt % of at least one compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof;

B. 1 to 20 wt % of a phosphorus acid ester and/or an amine thereof; and

C. 1 to 40 wt % of at least one compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof.

The lubricating oil concentrate of the present invention has a total phosphorus content in the range of 5,000 to 80,000 mass ppm.

In a further aspect, the present invention relates to a method of producing the lubricating oil composition of the present invention by blending the mixture of the components of the lubricating oil composition of the present invention. The resulting lubricating oil composition having excellent thermal stability, extreme pressure resistance and anti-wear performance.

In still a further aspect, the present invention relates to a method of lubricating hydraulic systems, bearing systems, gear systems, or sliding systems with the lubricating oil composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned above, the present invention relates to a lubricating oil composition for use in industrial oils such as hydraulic oils, bearing oils, industrial gear oils and sliding surface lubricating oils. The lubricating oil composition of the present invention provides excellent thermal stability, extreme pressure resistance and anti-wear performance. The lubricating oil composition of the present invention described herein having thermal stability will minimize sludge formation and viscosity increase resulting from decomposition of the components in the present invention.

The base oil of lubricating viscosity used in the lubricating oil composition of the present invention may be mineral or synthetic base oil having a kinematic viscosity of 5 to 900 mm^2/s, preferably 20 to 700 mm^2/s at 40 °C. A mineral oil employable for the invention can be obtained from crude oil by distillation (under atmospheric or reduced pressure) and purification such as solvent extraction, hydrocracking, solvent dewaxing or hydrogenation refining. Particularly preferred is a highly hydrogenation-refined base oil having a viscosity index of 100 to 150, an aromatic content of 5 wt % or less, a nitrogen content of 50 ppm or less, and a sulfur content of 50 ppm or less.

The synthetic oil (i.e., synthetic lubricating base oil) can be poly-α-olefin which is a polymer of α-olefin having 3 to 12 carbon atoms; a dialkyl diester such as dioctyl

sebacate, which is an ester of a dibasic acid (e.g., sebacic acid, azelaic acid, or adipic acid) and an alcohol having 4 to 12 carbon atoms; a polyol ester which is an ester of a monobasic acid having 3 to 18 carbon atoms and 1-trimethylolpropane or pentaerythritol, or an alkylbenzene having an alkyl group which contains 9 to 40 carbon atoms.

The mineral oil and synthetic oil can be employed singly or blended in combination. Blends of mineral oils with synthetic oils are also useful.

The lubricating oil composition of the present invention contains 0.1 to 5.0 wt %, preferably 0.1 to 3.0 wt %, more preferably 0.1 to 1.0 wt % and most preferably 0.1 to 0.5 wt %, of at least one compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and an amine salt thereof. The amount means a ratio based on the total amount of the lubricating oil, and each component of the indicated amount contains a small amount of hydrocarbon oil which is employed in the preparation of the component and remains in the component.

The phosphoric acid ester, thiophosphoric acid ester, and amine salt thereof functions to enhance the lubricating performances, and can be selected from known compounds conventionally employed as extreme pressure agents. Generally employed are a phosphoric acid ester, a thiophosphoric acid ester, or an amine salt thereof which has an alkyl group, an alkenyl group, an alkylaryl group, or an aralkyl group, any of which contains approximately 3 to 30 carbon atoms.

Examples of the phosphoric acid esters include aliphatic phosphoric acid esters such as triisopropyl phosphate, tributyl phosphate, ethyl dibutyl phosphate, trihexyl phosphate, tri-2-ethylhexyl phosphate, trilauryl phosphate, tristearyl phosphate, and trioleyl phosphate; and aromatic phosphoric acid esters such as benzyl phenyl phosphate, allyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, ethyl diphenyl phosphate, cresyl diphenyl phosphate, dicresyl phenyl phosphate,

ethylphenyl diphenyl phosphate, diethylphenyl phenyl phosphate, propylphenyl diphenyl phosphate, dipropylphenyl phenyl phosphate, triethylphenyl phosphate, tripropylphenyl phosphate, butylphenyl diphenyl phosphate, dibutylphenyl phenyl phosphate, and tributylphenyl phosphate. Preferably, the phosphoric acid ester is a trialkylphenyl phosphate.

Examples of the thiophosphoric acid esters include aliphatic thiophosphoric acid esters such as triisopropyl thiophosphate, tributyl thiophosphate, ethyl dibutyl thiophosphate, trihexyl thiophosphate, tri-2-ethylhexyl thiophosphate, trilauryl thiophosphate, tristearyl thiophosphate, and trioleyl thiophosphate; and aromatic thiophosphoric acid esters such as benzyl phenyl thiophosphate, allyl diphenyl thiophosphate, triphenyl thiophosphate, tricresyl thiophosphate, ethyl diphenyl thiophosphate, cresyl diphenyl thiophosphate, dicresyl phenyl thiophosphate, ethylphenyl diphenyl thiophosphate, diethylphenyl phenyl thiophosphate, propylphenyl diphenyl thiophosphate, dipropylphenyl phenyl thiophosphate, triethylphenyl thiophosphate, tripropylphenyl thiophosphate, butylphenyl diphenyl thiophosphate, dibutylphenyl phenyl thiophosphate, and tributylphenyl thiophosphate. Preferably, the thiophosphoric acid ester is a trialkylphenyl thiophosphate.

Also employable are amine salts of the above-mentioned phosphates and thiophosphates. Amine salts of acidic alkyl or aryl esters of the phosphoric acid and thiophosphoric acid are also employable. Preferably, the amine salt is an amine salt of trialkylphenyl phosphate or an amine salt of alkyl phosphate.

One or any combination of the compounds selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and an amine salt thereof may be used.

If the content of the phosphoric acid ester, thiophosphoric acid ester, and/or their amine salts in the lubricating oil is less than 0.1 wt %; the lubricating oil composition of the present invention will have insufficient lubricating performance. If the content

is more than 5.0 wt.%, no further improvement is expected and would not be cost-effective.

The lubricating oil composition of the present invention further contains 0.01 to 1.0 wt %, preferably 0.01 to 0.4 wt %, more preferably 0.01 to 0.2 wt %, and most preferably 0.01 to 0.1 wt %, of a phosphorus acid ester and/or an amine salt thereof. The amount means a ratio based on the total amount of the lubricating oil, and each component of the indicated amount contains a small amount of hydrocarbon oil which is employed in the preparation of the component and remains in the component.

In the lubricating oil composition of the present invention, the weight ratio between the compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof and the phosphorus acid ester and/or an amine thereof is in the range of 1:1 to 500:1, preferably 1:1 to 50:1, more preferably 1:1 to 25:1, and most preferably 1:1 to 10:1.

The phosphorus acid ester and/or its amine salt function to enhance the lubricating performances, and can be selected from known compounds conventionally employed as extreme pressure agents. Generally employed are a phosphorus acid ester or an amine salt thereof which has an alkyl group, an alkenyl group, an alkylaryl group, or an aralkyl group, any of which contains approximately 3 to 30 carbon atoms.

Examples of the phosphorus acid esters include aliphatic phosphorus acid esters such as triisopropyl phosphite, tributyl phosphite, ethyl dibutyl phosphite, trihexyl phosphite, tri-2-ethylhexylphosphite, trilauryl phosphite, tristearyl phosphite, and trioleyl phosphite; and aromatic phosphorus acid esters such as benzyl phenyl phosphite, allyl diphenylphosphite, triphenyl phosphite, tricresyl phosphite, ethyl diphenyl phosphite, tributyl phosphite, ethyl dibutyl phosphite, cresyl diphenyl phosphite, dicresyl phenyl phosphite, ethylphenyl diphenyl phosphite, diethylphenyl

phenyl phosphite, propylphenyl diphenyl phosphite, dipropylphenyl phenyl phosphite, triethylphenyl phosphite, tripropylphenyl phosphite, butylphenyl diphenyl phosphite, dibutylphenyl phenyl phosphite, and tributylphenyl phosphite. Also favorably employed are dilauryl phosphite, dioleyl phosphite, dialkyl phosphites, and diphenyl phosphite. Preferably, the phosphorus acid ester is a dialkyl phosphite or a trialkyl phosphite.

Amine salts of these phosphorus acid esters are also employable and can be used singly or together in combination.

If the content of the phosphorus acid ester and/or its amine salt in the lubricating oil is less than 0.01 wt %, the lubricating oil composition of the present invention will have insufficient lubricating performance. If the content is more than 1.0 wt %, no further improvement is expected and would not be cost-effective.

The lubricating oil composition of the present invention further contains 0.01 to 2.0 wt %, preferably 0.01 to 1.0 wt %, more preferably 0.01 to 0.4 wt %, and most preferably 0.01 to 0.2 wt %, of a compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzyl amine, and derivatives thereof. The amount means a ratio based on the total amount of the lubricating oil, and each component of the indicated amount contains a small amount of hydrocarbon oil which is employed in the preparation of the component and remains in the component.

In the lubricating oil composition of the present invention, the weight ratio between the phosphoric acid ester and/or an amine thereof and the compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof is in the range of 1:0.5 to 1:20, more preferably 1:1 to 1:3, and most preferably 1:1 to 1:2 wt %.

The alkenyl succinimide can be a monoimide or a bisimide, and can be prepared by reaction between a polybutenyl succinic anhydride and a polyamine. The

polybutenyl succinic anhydride can be produced by reaction of a polybutene having a mean molecular weight of 800 to 8,000 or a chlorinated polybutene having a mean molecular weight of 800 to 8,000 with maleic anhydride at a temperature of 100 to 200 °C. Examples of the polyamines include diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and hexamethylene heptamine.

Examples of the alkenyl succinimide derivatives include borated derivatives, organic phosphonate derivatives, and derivatives which is produced by reacting an alkenyl succinimide with aldehyde, ketone, carboxylic acid, sulfonic acid, alkylene oxide, sulfur, or polyhydric alcohol. A preferred derivative is a borated derivative, which can be produced by reacting the polybutenyl succinic anhydride-polyamine reaction product with boric acid or a boric acid derivative.

The alkenyl succinic acid ester and its derivative can be an ester of the above-mentioned polybutenyl succinic anhydride which has been prepared by the reaction between a polybutene or a chlorinated polybutene and maleic anhydride, with a polyhydric alcohol such as pentaerythritol, and its derivative.

The benzylamine and its derivative can be prepared by reacting the above-mentioned polybutene with phenol, formaldehyde and polyamine.

One or any combination of the compounds selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzyl amine, and derivatives thereof may be used.

If the content of the component in the lubricating oil is less than 0.01 wt %, sludge dispersing performance will be insufficient and, furthermore, the lubricating oil composition of the present invention will have poor water tolerance. If the content is more than 2.0 wt %, oxidation stability likely decreases.

The lubricating oil composition of the present invention has a total phosphorus content in the range of 50 to 5,000 mass ppm, preferably 50 to 2,500 mass ppm, and most preferably 50 to 1,000 mass ppm.

The lubricating oil composition of the present invention may contain a variety of other auxiliary additives that can be favorably employed in the present invention. Examples of the auxiliary additives include extreme pressure agents, corrosion inhibitors, rust inhibitors, friction modifiers, anti-foaming agents, viscosity index improvers and pour point depressants. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it.

The lubricating oil composition of the present invention can be prepared by successively or simultaneously adding the additive components to a base oil of lubricating viscosity, or by beforehand preparing a lubricating oil concentrate, as herein described below, and then mixing it with a base oil of lubricating viscosity. The components can be blended in any order and can be blended as combinations of components.

In a further aspect, the present invention also involves a lubricating oil concentrate comprising 1.0 to 30 wt % of a compatible organic diluent and

A. 10 to 90 wt % of at least one compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof;

B. 1 to 20 wt % of a phosphorus acid ester and/or an amine thereof; and

C. 1 to 40 wt % of at least one compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof.

The concentrates contain sufficient organic liquid diluent to make them easy to handle during shipping and storage. Typically, the concentrate will contain from 1.0 to 30.0 wt %, preferably 3.0 to 20.0 wt %, more preferably 5.0 to 10.0 wt %, of a compatible organic diluent.

Suitable compatible organic diluents which can be used include, for example, solvent refined 100N, i.e., Cit-Con 100N, and hydrotreated 100N, i.e., Chevron 100N, and the like. The organic diluent preferably has a viscosity of about from 1.0 to 20.0 cSt at 100°C.

In the lubricating oil concentrate of the present invention, the weight ratio between the compound selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and amine salts thereof and the phosphorus acid ester and/or an amine thereof is in the range of 1:1 to 500:1, preferably 1:1 to 50:1, more preferably 1:1 to 25:1, and most preferably 1:1 to 10:1.

In the lubricating oil concentrate of the present invention, the weight ratio between the phosphoric acid ester and/or an amine thereof and the compound selected from the group consisting of an alkenyl succinimide, an alkenyl succinic acid ester, benzylamine, and derivatives thereof is in the range of 1:0.5 to 1:20, more preferably 1:1 to 1:3, and most preferably 1:1 to 1:2 wt %.

The lubricating oil concentrate of the present invention has a total phosphorus content in the range of 50 to 5,000 mass ppm, more preferably 10,000 to 50,000 mass ppm, and most preferably 15,000 to 30,000 mass ppm.

EXAMPLES

The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it. This application is intended to cover those various changes and substitutions that may be made by

those skilled in the art without departing from the spirit and scope of the appended claims.

Examples 1-4

The components were blended in amounts (wt %) set forth in Table I to prepare lubricating oil compositions.

(A) Tricresyl phosphate solution: TCP (available from Daihachi Chemicals Co., Ltd.)

(B) Triphenyl thiophosphate and its derivative solution (Irgalube 232, available from Ciba Specialty Chemicals, Inc.)

(C) Dilauryl phosphite solution (JP 212, Johoku Chemicals Co., Ltd.)

(D) Alkenylsuccinimide (OLOA 371, available from Chevron Oronite Japan Ltd.)

(E) Zinc dithiophosphate (OLOA 269R, available from Chevron Oronite Japan Ltd.)

Each of the components above were blended in a petroleum base oil having a viscosity @ 40°C of 36 cSt containing auxiliary additives, i.e., oxidation inhibitor, metal deactivator, demulsifier, anti-foaming agent, etc. The total phosphorus contents (mass ppm) were those set forth in Table I.

Comparative Examples A-G

The above-mentioned additive components were blended to prepare lubricating oil compositions as described in the Examples. The amounts of each of the components in the Comparative Examples are indicated in Table I.

Performance Evaluation

The lubricating oil compositions of Examples and Comparative Examples were evaluated by the following tests. The results of the tests are set forth in Table II.

Modified CM Thermal Stability Test

The lubricating oil compositions were evaluated by a modified CM Thermal Stability Test that heated the composition at 150 °C rather than at 135 °C under the following conditions:

Test temperature: 150°C

Test period: 168 hours.

The test oil was then filtered over a filter (pore size: 0.8 μm), washed with n-hexane, and dried. The dry residue on the filter was weighed to determine the amount of sludge. The lower the number (mg), the lower the sludge. The viscosity increase is also indicated. A viscosity increase lower than 5% is preferable.

Shell Four-Ball Test

The lubricating oil compositions were evaluated by the Shell Four-Ball Tester, which operated at 1,800 r.p.m., to determine an initial seizure load (ISL). The higher the number (kg), the better the extreme pressure resistance.

Vickers 35VQ25A (M-3952-5)

The Vickers 35VQ25A (M-3952-5) vane pump test is a common wear test to evaluate the anti-wear characteristics of hydraulic oil by means of weight loss on the cam ring and the vanes of a 35VQ25A pump. Test duration is 50 hours per cartridge

with a pump outlet pressure of 3,000 psi and an inlet oil temperature of 93.3 °C. A low number indicates low wear.

Table I[1]

	(A)	(B)	(C)	(D)	(E)	Phosphorus Content, ppm
<u>Examples</u>						
1	0.200	-	0.025	0.050	-	180
2	0.400	-	0.050	0.100	-	360
3	-	0.200	0.025	0.050	-	160
4	0.200	-	0.025	0.050	-	160
<u>Comparative Examples</u>						
A	0.200	-	-	-	-	160
B	0.200	-	-	0.050	-	160
C	0.200	-	0.025	-	-	180
D	-	-	0.025	-	-	20
E	-	-	0.025	0.050	-	20
F	0.5	-	-	-	-	420
G	-	-	-	-	0.4	300

[1] Each of the above Examples and Comparative Examples were blended in a petroleum base oil having a viscosity @ 40 °C of 36 cSt, containing auxiliary additives, i.e., oxidation inhibitor, metal deactivator, demulsifier, anti-foaming agent, etc.

Table II

	Modified CM Thermal Stability Test		Shell Four-Ball Test	Vickers 35VQ25A (M-3952-5)	
	Sludge mg	Viscosity increase %	ISL kg	Ring mg	Valve mg
Examples					
1	1.0	5	80	-	-
2	1.4	2	100	-	-
3	1.0	0	80	-	-
4	-	-	-	25.3	1.7
Comparative Examples					
A	0.8	5	63	-	-
B	1.0	7	63	-	-
C	1.9	6	80	-	-
D	1.9	8	80	-	-
E	0.5	10	63	-	-
F	-	-	-	2,083	21
G	-	-	-	64.1	6.2

Results of the three test evaluations are shown in Table II. In general, the lubricating oil composition of the present invention produces sludge and viscosity increase less than the Comparative lubricating oil compositions, while also providing excellent extreme pressure resistance. That is, the lubricating oil compositions of the present invention showed a high initial seizure load in the Shell Four-Ball Test, which means excellent extreme pressure resistance. While some of the Comparative Examples gave modified CM Thermal Stability Test results comparable to the Examples, they did not provide favorable viscosity increase or extreme pressure resistance. See for example, Comparative Example E. Further, Comparative Examples C and D provided excellent extreme pressure resistance, but the thermal stability and viscosity increase were higher than the lubricating oil compositions of the present invention demonstrated by Examples 1-3. Additionally, the lubricating oil composition of the present invention (Example 4) also demonstrated excellent anti-wear performance in the Vicker 35VQ25A (M-3952-5) Test.

These results therefore provide support that the lubricating oil composition of the present invention has a broader scope of lubricating performance than the comparative lubricating oil compositions. The lubricating oil composition of the present invention provides an excellent combination of thermal stability, extreme pressure resistance and anti-wear performance all in one multi-functional package.